

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
27 June 2002 (27.06.2002)

PCT

(10) International Publication Number  
**WO 02/50184 A2**

(51) International Patent Classification<sup>7</sup>: C08L 63/00, C08G 59/22, 59/40

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(21) International Application Number: PCT/US01/48718

(22) International Filing Date: 14 December 2001 (14.12.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 60/257,321 20 December 2000 (20.12.2000) US

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**WO 02/50184 A2**

(54) Title: COMPOSITIONS FOR VIBRATION DAMPING

(57) Abstract: A vibration damping composition including (a) at least one saturated thermosettable component such as a polyurethane precursor, or an epoxy resin having one or more epoxy groups; (b) a crosslinking agent for the saturated thermosettable component; and (c) a thermoplastic interpolymer resin such as a  $\alpha$ -olefin/vinyl aromatic interpolymer, for example an ethylene-styrene interpolymer (ESI); wherein the glass transition temperature of the cured saturated thermosettable component is between -20 °C and +100 °C; and the vibration damping composition provides efficient damping at 0-60 °C with a maximum damping factor >15 percent that is stable at 0-30 °C.

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## COMPOSITIONS FOR VIBRATION DAMPING

This invention relates to resin compositions useful for damping vibration  
5 applications, and more particularly, this invention relates to saturated thermosettable components blended with crosslinking agents and thermoplastic  $\alpha$ -olefin/vinyl aromatic interpolymers, such as ethylene-styrene interpolymers (ESI), wherein such blends are useful for applications where damping of vibrations are required.

There are various applications where a vibration damping material may be  
10 used including for example transportation vehicles, electronic device apparatuses and machines which contain a vibration source such as a motor. Various vibration damping materials have heretofore been proposed for attenuating vibrations caused by a vibration source, most typically, from an engine of a vehicle, with varying degrees of success.

Heretofore, the automotive industry has been searching for vibration  
15 damping products that would provide damping factors greater than 15 percent at operating temperatures conditions typically 0 °C – 50 °C. Currently available bituminous membranes, which are standard products used for damping vibration in cars, have a vibration damping factor below 15 percent. A 10 percent damping factor is the minimum generally recognized level for efficient damping performance in the automotive industry.

20 The use of epoxy resins in formulations for damping vibrations, particularly for the automotive industry, is described in PCT Patent Application Publication No. WO 99/16840. WO 99/16840 describes a system developed for automotive underbody coating and shows examples of damping factors, superior to 20 percent, as measured according to the method DIN 53440, Part 1 [*Testing of plastics and damped laminated systems; bending vibration test; general rudiments of dynamical elastic properties of bars and strips*].  
25 Method DIN 53440 is equivalent to SAE J1637, another often used procedure by those skilled in the art. This method allows one to determine the loss factor of a material applied to a metal bar of defined surface area (about 22 cm<sup>2</sup>). The resulting loss factor is expressed as a percentage.

30 However, the damping performance of the product described in WO 99/16840 is efficient only in a rather narrow range or band width of temperatures when formulated with usual fillers such as calcium carbonate (typically from 10 °C to 30 °C for a loss factor at 200 Hertz (Hz) above 10 percent, that is a band temperature width of only 20 °C). More expensive fillers with high aspect ratio such as mica are needed to expand the

useful temperature range for damping. Also, relatively high level of epoxy resin (about 50 percent in the formulation) are generally used to obtain high loss factors. It is desirable to expand the temperature range in which the vibration damping performance stays above 10 percent at a lower formulation cost.

5        It is also desired to provide a composition which will meet the automotive industry's damping requirements, which when further blended with thermoplastic resins provide excellent vibration damping performance over a wider temperature range, and which will include components such as epoxy resins and crosslinking agents that are classified as non-hazardous to humans by skin contact (the compositions described in WO  
10      99/16840 require the use of epoxy resins labeled irritant, with risk phrase "R=43: May cause sensitization by skin contact."

The present invention is directed to a vibration damping composition including:

- (a) at least one saturated thermosettable component such as but not limited to  
15      (i) an epoxy resin having one or more epoxy groups or (ii) a polyurethane precursor;
- (b) a crosslinking agent and/or curing catalyst for the saturated thermosettable component, such that upon curing of the saturated thermosettable component, the resultant cured thermoset product has a glass transition temperature (Tg), as measured by differential scanning calorimetry (DSC), in the range of from -20 °C to 85 °C;
- 20      (c) a thermoplastic interpolymer resin having a Tg in the range of from -20 °C to 40 °C;

wherein the concentration of the saturated thermosettable component, the crosslinking agent and the thermoplastic interpolymer resin is sufficient to provide a composition having a loss factor above 10 percent over an entire temperature band width of  
25      50 °C; and 15 percent over a temperature band width of 30 °C; and

- (d) optionally, one or more fillers, pigments and/or other additives.

In one preferred embodiment, pastes made from the compositions of the present invention are useful in automotive applications because such compositions are resistant to automotive treatment processes and corrosion; and may replace the standard  
30      bituminous membranes currently used in the automotive industry allowing for automation in the automotive manufacturing process.

Figure 1 is a graphical illustration showing the damping performance of a composition of the present invention with and without ethylene-styrene interpolymer (ESI).

5 Figure 2 is a graphical illustration showing the effect of different ESI levels on the damping performance.

Figure 3 is a graphical illustration showing the damping performance of a composition of the present invention over 50 °C temperature width (range from 0 °C to 50 °C typical of an automotive use).

In its broadest scope, the composition of the present invention includes a  
10 combination or blend of (A) a mixture of (i) one or more saturated thermosettable components such as polyurethane precursors, or epoxy resins having one or more epoxy groups and (ii) a crosslinking agent for such saturated thermosettable components; and (B) one or more thermoplastic interpolymer resins such as ethylene-styrene interpolymer (ESI).

“Saturated thermosettable components” include all resins which crosslink via  
15 any chemical reaction other than the polymerization of unsaturated carbon-carbon multiple bonds.

The composition of the present invention is advantageously used as a vibration damping material having damping performance within a temperature range of from -20 °C to 100 °C. While the automotive industry is in need of an efficient vibration  
20 damping material at and around ambient temperature, it is contemplated that the systems of the present invention may be used for other than automotive applications such as for example lawn and garden tractors, air conditioner housings, and other end uses.

A preferred embodiment of the present invention includes the use of at least one or more risk-label-free saturated thermosettable components and crosslinking agents in  
25 which  $\alpha$ -olefin/vinyl aromatic interpolymers are incorporated or dispersed therein, together with fillers, pigments and optionally other additives such as curing catalysts, thickeners, rheology modifiers (all well known by the formulators skilled in the art, supplying such systems), to make a composition in the form of a liquid to a high viscous paste or mastic that can be applied to a substrate to form a coating.

30 The formulated compositions of the present invention offer efficient damping over a wider temperature range, more specifically between 0 °C and 50 °C, with a maximum loss factor of 22 percent, and a value that stays above 15 percent over 30 °C due to the

combination of the saturated thermosettable resin and the  $\alpha$ -olefin/vinyl aromatic interpolymers.

Optionally, the composition of the present invention can be designed to provide an efficient vibration damping performance as defined above by the loss factor over 5 a broad temperature window of at least 30 °C wide and preferably at least 50 °C wide, centered at an elevated temperature above ambient (about 20 °C) and below 70 °C. For such a purpose, both the cured thermoset component and the thermoplastic interpolymer of the composition are selected to have their glass transition temperature and/or maximum of dynamic loss modulus in the temperature range where vibration damping is required. Such 10 a system is particularly suitable for applications, machines or apparatuses operating at temperatures above ambient up to 100 °C.

In general, the difference between the Tg of the cured thermoset component and the Tg of the thermoplastic interpolymer ( $\Delta$ Tg) does not exceed 50 °C, preferably does not exceed 30 °C, and more preferably does not exceed 20 °C.

15 The coating compositions of the present invention can be applied to steel or other substrate on automotive body parts before assembling, but heat curing is generally delayed until the car body enters the paint curing ovens later on the assembly line. In this case, the coating is applied in form of a high enough viscous paste to be resistant to the typical automotive body treatment processes of the painting line, meaning not being washed 20 away and not contaminating the treatment bath. Usual metal treatments include various degreasing, washing, acid or base metal treatment steps (phosphatation and passivation steps performed at up to 45 °C, by applying water solutions in form of jets or bath), followed by the electrodeposition of the cathodic electrodeposition (CED) primer, prior to the cure of the compositions of the present invention at a cure temperature of 155 °C to 200 °C for 30 25 minutes to 60 minutes in the CED primer curing ovens. The coatings of the present invention also fulfill the requirements of corrosion testing methods for the automotive industry including methods D17 15058, D17 1686 and D45 1148 (Peugeot-Renault normalized test methods). For example, the cured epoxy resin and the thermoplastic 30 interpolymer resin are such that their glass transition temperature can be between 0 °C and 60 °C, which defines the range of damping and make the materials particularly suitable and unique for this application.

The formulations of the present invention are novel because of (i) the unique combination of a saturated thermosettable component with a thermoplastic interpolymer

such as ESI, (ii) the fact that the formulations of the present invention have an effective damping performance (loss factor at 200 Hertz (Hz) is greater than 10 percent over a broad temperature range of at least 30 °C, preferably up to 50 °C, (iii) the fact that the formulations of the present invention are better performing than bituminous membranes which have a maximum damping factor of 15 percent and which are currently used in the automotive industry today, and (iv) the fact that the formulations of the present invention can be "non-hazardous" (that is non-irritating/non-sensitizing by skin contact and as such are risk-label-free for classification and labeling of preparations as outlined in the European Dangerous Preparations Directive 88/379/EEC and its amendments. Bisphenol-A based epoxy resins with a molecular weight below 700 (CAS # 25068-38-6) are listed in Annex I of the European Dangerous Substance Directive 67/548/EEC and classified as irritant (hazard symbol "Xi") and dangerous to the environment (hazard symbol "N") with the risk phrases "R36/38" (irritating to eyes and skin), "R 43" (may cause sensitization by skin contact) and "R 51/53" (toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment). Bisphenol-A based epoxy resins with a molecular weight above 700 do not require classifications according to EU legislation. The automotive industry prefers risk-label-free systems.

In a preferred embodiment of the present invention, the composition is used in the form of a paste. The paste of the present invention may replace advantageously for example, bituminous membranes currently used in the automotive industry.

Advantageously, a coating paste can be applied by automated processes which is a key driver in the automotive industry. For example, the paste may be applied to a substrate by robotic application eliminating the need for manual application of bituminous membranes to a substrate.

The polyurethane precursors useful in the present invention as the saturated thermosettable component may be a resin such as a polymer and/or a blend of polymers, including for example, polyoxypropylene diols/triols, polyester polyols, polyether polyols, hydroxy functional polyurethane prepolymers and mixtures thereof.

The formulation of the present invention further comprises a crosslinking agent for the polyurethane precursors. The crosslinking agent for the polyurethane precursor includes essentially an isocyanate, a polyisocyanate, an isocyanate functional polyurethane prepolymer and mixtures thereof.

The crosslinking agent reacted with the polyurethane precursor forms a polyurethane resin system. More particularly, the system may include the reaction product of an amine terminated polyether (selected from aminated diols or triols, well described in U.S. Patent No. 3,654,370). Particularly recommended amine terminated polyether products 5 useful in the present invention are the Jeffamine brand series from Hunstman Petrochemical Corporation that is Jeffamine D-2000, D-4000, T-3000, T-5000, T-403 or T-230) or a hydroxy-terminated polyether (polyether polyol i.e VORANOL\* 230, VORANOL\* 220 available from The Dow Chemical Company (\*VORANOL is a registered trademark of The Dow Chemical Company), or blends of the two as an active hydrogen-containing material 10 and an isocyanate compound such as an aromatic or an aliphatic compound, widely described in U.S. Patents Nos. 4,705,814; 2,683,730; and 3,362,979. One example of an isocyanate used in the present invention is methylene bis(4-phenylisocyanate or commonly called "MDI" which is used to form a polyurea, polyurethane or hybrid elastomer. Another example of the isocyanate is toluene diphenyl diisocyanate.

15 Generally, the total amount of polyurethane precursor and the crosslinking agent used for the precursor is from an amount of 20 percent by weight to 80 percent by weight, preferably 25 percent by weight to 60 percent by weight, and more preferably 40 weight percent or less based on the weight of the formulation.

20 The crosslinking agent used for the polyurethane precursor in the present invention is generally present at a stoichiometric amount – ratio hydroxyl groups to active hardener groups - from 1.5 to 0.7, preferably from 1.2 to 0.8, and more preferably from 1.1 to 0.9.

25 Any epoxy resin having one or more epoxy groups known by those skilled in the art may be used in the present invention as the thermosettable component of the present invention. The specific epoxy resin selected can include aromatic and aliphatic types, and mixtures thereof. However, important in developing a formulation which has good vibration damping performance and which is of the risk-label-free type, is the selection of the epoxy resins used in the formulation.

Preferred aromatic epoxy resins are epoxy resins having bisphenol moieties 30 in the backbone of the epoxy resin. Representative of preferred bisphenol resins useful in this invention are those disclosed in U.S. Patent No. 5,308,895 at column 8, line 6 and represented by Formula 6. The most preferred aromatic epoxy resins are bisphenol-A based epoxy resins and bisphenol-F based epoxy resins.

In a more preferred embodiment of the present invention, bisphenol-A based epoxy resins are used. For example, the resins may be straight reaction products of diglycidyl ether of bisphenol-A (DGEBA) and bisphenol-A (bis-A). A typical epoxy resin product used in the present invention is D.E.R.\* 661E (1 -Type Bisphenol-A epoxy resin),  
5 available from The Dow Chemical Company. (\* D.E.R. is a registered trademark of The Dow Chemical Company).

In another embodiment of the present invention, the epoxy resins can be, for example, the reaction product of DGEBA, bis-A and a fatty acid and/or a dimer fatty acid derived from a natural oil such as for example linseed, tall, or castor oil fatty acids. Those  
10 resins are typically high viscous to solid and the process for making these resins are described in column 8, line 6 of U.S. Patent No. 5,308,895. Such fatty acid modification of a bisphenol-A epoxy resin, as well as other known modifications, permit the adjustment of the temperature range of the vibration damping efficiency in the final cured product.

The preferred aliphatic epoxy resins useful in the present invention are  
15 derived from polyether chains which are preferably prepared from one or more alkylene oxides. Representative examples of these aliphatic epoxy resins are those described in U.S. Patent No. 5,308,895 at column 8, line 9 and formula 9 and the description thereof following. Preferably, the aliphatic epoxy resin contains in its backbone ethylene oxide, propylene oxide or a mixture thereof.

20 More preferably, aliphatic liquid epoxy resins specifically include D.E.R.\* 732 epoxy resin (process described in column 8, line 9 of U.S. Patent No. 5,308,895) or other suitable monofunctional or polyfunctional liquid epoxy products such as epoxidized oils, dimer fatty acid diglycidyl ester, or epoxidized cashew nut oil, all commercially available. Preferred aliphatic epoxy resins also include, for example, D.E.R.\* 736 epoxy  
25 resin available from The Dow Chemical Company. (\*D.E.R. is a registered trademark of The Dow Chemical Company).

The epoxy resin may also include a mixture of a bisphenol A type epoxy resin and an aliphatic epoxy resin. The epoxy resins useful in the present invention can also include, for example the epoxy resins described in PCT WO 99/16840 which are described  
30 as flexible epoxy resins and rigid epoxy resins, and may be used as a mixture in a ratio that achieves the desired results. Preferably, the more flexible aliphatic epoxy resin is used in

combination with the more rigid bisphenol-A based epoxy resin in a ratio which adjusts the temperature range of the vibration damping efficiency in the final cured product.

In another embodiment of the present invention, the aliphatic epoxy resin can be included as a reactive partner during the manufacturing process of the bisphenol-A based 5 epoxy resin together with the DGEBA and bisphenol-A reactants. In this case aromatic-aliphatic hybrid epoxy resin structures are obtained.

The average number molecular weight ( $M_n$ ) of the bisphenol-A based epoxy resin is generally from 350 to 5000. In one preferred embodiment, to comply with the non-skin-sensitizing requirement, the epoxy resin molecular weight is greater than 700, 10 preferably greater than 800, and more preferably greater than 900. Typically, the range of the molecular weight of the epoxy resin is generally from 800 to 5000, preferably from 900 to 3000, and more preferably from 900 to 2000.

Typically, the range of the molecular weight of the aliphatic liquid epoxy resin is generally from 300 to 4000, preferably from 500 to 2000, and more preferably from 15 500 to 1000. In the preferred embodiment wherein a non-sensitizing skin composition is required, the aliphatic epoxy resins present in the composition of the present invention is preferably selected amongst liquid aliphatic resins commercially available which are recognized non-irritating and non-sensitizing by skin contact.

The cured dampening compositions are characterized by Dynamic 20 Mechanical Thermal Analysis (DMTA). The Differential Scanning Calorimetry (DSC) method for Tg measurement is not sensitive enough for such complex filled systems. It also has to be recognized that the Tg by DMTA is always greater by about 15 or more °C than the Tg measured by DSC.

The epoxy resins used in the present invention should be such that the glass 25 transition temperature (Tg) of the cured formulation, as determined by DMTA (Tg is given by the temperature at the maximum of peak Tan delta (mechanical loss factor) which is defined as the ratio of loss to storage modulus), is -5 °C or greater, preferably 10 °C or greater, and more preferably 20 °C or greater. Preferably the DMTA glass transition temperature peak is at 100 °C or less and more preferably 80 °C or less. In a preferred 30 embodiment, the mechanical loss factor Tan delta measured at 10 Hertz (Hz) should be a broad and high peak with respect to temperature, preferably the width of the peak at half height is greater than 30 °C and more preferably 50 °C.

Preferably, the epoxy resin is present in the formulation in an amount of 20 percent by weight or greater, more preferably 25 percent by weight or greater based on the weight of the formulation.

Preferably the epoxy resin is present in the formulation in an amount of 80  
5 weight percent or less, more preferably 60 percent by weight or less and even more  
preferably 40 weight percent or less based on the weight of the formulation.

Preferably, the epoxy resins or blends of epoxy resins are liquid at a  
temperature between 20 °C and 50 °C which is a typical temperature range for  
manufacturing a formulation. In general, the viscosity of the epoxy resin at the processing  
10 temperature is lower than 60 Pa.s, preferably lower than 30 Pa.s, and even more preferably  
lower than 10 Pa.s.

The formulation of the present invention further comprises a crosslinking  
agent for the epoxy resin. The crosslinking agent (which will also be interchangeably  
referred to herein as a "curing agent" or "hardener") can be any curing agent useful with  
15 epoxy resins and known to one skilled in the art.

Almost all known curing agents for epoxy resins can be used. For one-component systems, a latent curing agent is preferably used. By "latent curing agent" it is meant that the curing reaction of the composition is induced at an elevated temperature above ambient and the formulated composition can be stored for a defined period of time  
20 (shelf-life) at low temperature, preferably at ambient temperature.

The curing agent used will depend on the application process and curing conditions. For example, for the high temperature cure of a one-component paste, a latent hardener which cures at elevated temperature is more suited, most preferred latent hardener is dicyandiamide, optionally associated with a latent curing catalyst.

For two-component formulations which are mixed prior to application, a low temperature curing hardener is preferred to permit the saturated thermosettable resin to cure at ambient temperature. Preferred ambient cure hardeners are polyamines of the aliphatic, cycloaliphatic or aromatic types. Such two-component formulations are, for instance, particularly suited to the building and civil engineering industry.  
25

Representative curing agents are disclosed in U.S. Patent No. 5,308,895 at column 11, line 8 to column 12 line 47. More preferably the curing agent is an amine terminated polyether, such as Jeffamine (trademark) amine terminated polyether available  
30

from Huntsman Chemical (for example Jeffamine 230), Eurodur (trademark) from Ciba Speciality Chemicals (for example Eurodur 70, 75 or 76), anhydrides, including dianhydrides, and cyandiamides or dicyandiamides and derivatives thereof. Most preferred curing agents are the dicyandiamides and the derivatives thereof.

5       The choice of the curing agent will effect the form of the composition, that is, determine whether it is a one-part or a two-part composition; shelf stability; final performance properties; and the curing temperature of the composition. For a two-component composition, a polyamine hardener or an amine terminated polyether or an anhydride curing agent is preferably used. For a one-component formulation, a  
10      dicyandiamide curing agent is preferably used.

The curing agent used in the present invention is generally present at a stoichiometric amount – ratio epoxy groups to active hardener groups - from 1.5 to 0.7, preferably from 1.2 to 0.8, and more preferably from 1.1 to 0.9.

Preferably, the thermoplastic interpolymer resins useful in the present  
15      invention are  $\alpha$ -olefin/vinyl or vinylidene interpolymers. The generic class of materials of  $\alpha$ -olefin/vinyl or vinylidene monomer, substantially random interpolymers, including materials such as substantially random  $\alpha$ -olefin/vinyl aromatic monomer interpolymers, and their preparation, are known in the art, such as described in U.S. Patent No. 5,703,187 (EP 416,815 A2), and in U.S. Patent No. 5,872,201.

20       The thermoplastic resins of the present invention include interpolymers derived from ethylene and/or  $\alpha$ -olefin monomers and vinyl or vinylidene monomers. Monomers that are acceptable for use in the interpolymers of the present invention include, for example, ethylene and/or any  $\alpha$ -olefin and any vinyl or vinylidene monomer. Suitable  $\alpha$ -olefins include, for example,  $\alpha$ -olefins containing from 3 to 20, preferably from 3 to 12,  
25      more preferably from 3 to 8 carbon atoms. Particularly suitable  $\alpha$ -olefins useful in the present invention are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1, octene-1 and mixtures thereof. These  $\alpha$ -olefins do not contain an aromatic moiety.

30       Examples of useable vinyl or vinylidene monomers include vinyl or vinylidene aromatic monomers, cycloaliphatic monomers, and any sterically hindered vinyl or vinylidene monomers. The interpolymers of the present invention may also include one or more additional polymerizable ethylenically unsaturated monomers.

Suitable vinyl or vinylidene aromatic monomers, which can be employed to prepare the interpolymers used in the compositions of the present invention, include, for example, styrene, vinyl toluene,  $\alpha$ -methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and mixtures thereof. Particularly suitable monomers 5 include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene,  $\alpha$ -methyl styrene, the lower alkyl- ( $C_1 - C_4$ ) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof. A more preferred aromatic vinyl or vinylidene monomer is styrene.

10 The most preferred substantially random interpolymers for use in the present invention are the ethylene/styrene and ethylene/propylene/styrene interpolymers.

Preferably, the thermoplastic resin is present in the formulation in an amount of 10 percent by weight or greater, more preferably 20 percent by weight or greater based on the weight of the formulation. Preferably the thermoplastic resin is present in the 15 formulation in an amount of 80 weight percent or less, more preferably 60 percent by weight or less and even more preferably 40 weight percent or less based on the weight of the formulation.

In order to be properly incorporated into the paste, the interpolymer is 20 preferably in a powder form. The size of the particles of the powder is generally 500 microns or less, preferably 300 microns or less, and more preferably 200 microns or less. The interpolymer can be cryogenically ground if needed.

The composition of the present invention may further comprise a catalyst for the reaction of the thermosettable component and the crosslinking agent. For example, in the system comprising an epoxy resin reacted with an epoxy curative compound; such 25 catalysts are well known to those skilled in the art, and include those described in U.S. Patent No. 5,344,856. The preferred classes of catalysts are the ureas, imidazoles, and boron trihalides with the ureas being the most preferred catalysts. Examples of urea type catalysts are: Dyhard 500 (TDI-uron, Cas N° 17526-94.2 from SKW Trostberg). Of the boron trihalides, boron trifluoride is the most preferred because formulations using this 30 catalyst demonstrate significantly better stability when compared to other boron trihalides.

For example, in the system comprising the reaction of a polyurethane precursor with a crosslinking agent for such precursor to form a polyurethane resin, such catalysts are well known and described for example in U.S. Patent No. 3,654,370.

The catalyst amount used may vary depending upon the desired reactivity and shelf stability. Preferably, when a catalyst is used, the catalyst is generally present in an amount of 0.05 to 5.0 weight percent, and preferably in an amount of 0.10 to 1.0 weight percent based on the weight of the formulation.

5       The formulation of the present invention may further comprise one or more fillers. The pastes of the present invention may optionally contain, for example, inorganic fillers such as CaCO<sub>3</sub>, CaO; and/or rheology additives such as carbon black and silica.

Fillers are used to control the viscosity, rheology, shelf stability, specific gravity and cured performance properties, such as vibration damping, corrosion resistance, 10 impact resistance and abrasion resistance. The fillers may be spherical or platy. As used herein "platy" means the particles have a high aspect ratio. High aspect ratio fillers include as talc, mica and graphite. Preferred high aspect ratio fillers include Phlogopite mica having a median particle size of 20 to 70 microns (micrometers) and most preferably 50 microns (micrometers). High aspect ratio fillers are used to control vibration damping 15 properties. Spherical fillers include carbonates. Spherical fillers are used to control density and rheology, viscosity and cost. Preferably, the filler is present in an amount of 0 percent by weight or greater, and more preferably 30 percent by weight or greater. Preferably, the filler is present in an amount of 65 percent by weight or less and more preferably 55 percent by weight or less.

20       The percentage of filler that can be included in the composition of the present invention on a weight basis is primarily a function of the density of the filler. Particle size and shape of the filler also will effect the properties of the composition. For example, ultra fine particle size fillers (less than 1 micron average particle size) generally have a tendency to result in higher blend viscosities and are also more expensive. The preferred filler useful 25 in the present invention is calcium carbonate.

The use of many types of fillers or combination thereof is, of course, possible without altering the fundamentals taught herein. For example, inclusion of alumina trihydrate (ATH, Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O) is highly desirable when flame-retardant or low-smoke-tendency blends are desired. Heavy fillers, such as powdered iron or lead, or 30 oxides or shavings of them, can be employed when ultra-dense blends are desired. Similarly, minerals having low density, such as magnesium carbonate, magnesium oxide, magnesium hydroxide, calcium sulfate, silica, fly ash, and cement dust, or organic fillers

such as yarns, wood flour, nut shells, rice hulls, cornmeal, and clay can be employed when light-density blends are preferable. Finally, fillers with varied aspect ratios, such as talc, mica, from highly acicular (wollastonite, for example) to round (glass beads, for example) can also be employed to alter relationships such as tensile strength or elongation.

5       The formulation of the present invention may further contain other additives well-known to those skilled in the art of making vibration dampening formulation. For example an adhesion promoter such as epoxy functional trimethoxy silanes, a thixotrope agent such as fumed silica or carbon black, or a plasticizer may be used, in well known amounts (typically from 0 to 5 weight percent) to modify rheological properties of the  
10      composition to a desired consistency.

The formulation of the present invention is preferably a liquid to a high viscous paste or mastic that can be applied by all known coating techniques. For example, the composition may be applied by spraying, by a tool such as a blade or a trowel, or by extrusion (for example a mastic). By "extruded" herein it is meant that the application of  
15      the paste onto a substrate is performed by pumping and the paste is forced to flow through a heated applicator gun under pressure. This technique can be easily automated. In another embodiment, a sheet or film of the formulation may be made by well-known methods and used in such form in vibration dampening application by adhering and curing onto the substrate.

20       The present invention formulations, based on blends of risk-label-free (as outlined in the European Dangerous Preparations Directive 88/379/EEC and its amendments for classification and labeling of preparations that is MW above 700) bisphenol-A epoxy resins and/or aliphatic epoxy resins with ethylene-styrene interploymer (ESI), give a maximum loss factor above 20 percent for 3.9 kg/m<sup>2</sup> applied weight (DIN 53440 Test  
25      method), while the bituminous membranes used widely today for damping vibrations in cars have a damping factor of maximum 15 percent (for 4.5 kg/m<sup>2</sup> applied weight). The present invention formulation is also better than another known type of paste, being commercialized, which is a rubber containing sulfur vulcanizing agents: Betaphon AV 50 (Trademark of Gurit-Essex), having a maximum loss factor of 15 percent.

30       Generally, the maximum loss factor of the formulations of the present invention range from 15 percent to 25 percent. More preferably the maximum loss factor is greater than 20 percent.

Generally, the amount of the formulation of the present invention applied to a substrate to form a coating from the formulations of the present invention range from 2 kg/m<sup>2</sup> to 5 kg/m<sup>2</sup>, and preferably from 3 kg/m<sup>2</sup> to 4 kg/m<sup>2</sup>.

The primary application of the present invention is directed to the use of 5 formulations as vibration damping products for doors, roofs, rear panels and other non-horizontal body parts in cars.

Advantageously, the use of ESI powder for the manufacture of the paste of the present invention allows for shorter cycle times in mixers useful for preparing the paste, as the needed homogeneity of the paste during the mixing is obtained 3 to 4 times faster 10 compared to known similar high viscous pastes (typically Betaphon AV 50 mentioned above). This is probably due to the rheological characteristics and interaction of the epoxy with the ESI that allows to obtain, after much shorter mixing times, a very high viscous highly filled homogenous mixture when a part of the epoxy resin is slowly incorporated into the dry components (fillers, ESI dry powder and other solid components). This is known in 15 the industry as "hard state" of highly filled pre-mix, before of the remainder liquid epoxy is incorporated into the mixture to reach final desired paste consistency.

Also, the present invention formulations, contrary to sulfur-vulcanized rubber pastes, do not give any odor release, neither to the automotive plant environment during application and curing, nor to the car inside environment as the pastes usually are 20 applied to the internal side of the body panels being treated. This is an advantage of the present invention chemistry versus the prior art vulcanized rubber based chemistry, particularly since the automotive industry is very concerned about release of odors and volatile into the finished car environment.

The process of the present invention involves contacting the formulation with 25 a substrate. The substrate can be any substrate for which vibration damping or abatement associated with the required level of corrosion protection is desired. Such substrate can be metal, wood, plastic, and fiber reinforced plastic. The formulation can be used in a wide variety of industries including the automotive industry, the transportation industry (public transportation, rail, navy etc...), in the appliance industry, in energy production, more 30 generally speaking in any industry or activity where moving or rotating parts create vibrations that need to be damped or attenuated together with the noise generated. To this also belongs the construction industry and associated equipment such as air conditioning units, heaters, ventilation systems.

Once the formulation is contacted with the substrate, the formulation is allowed to cure. For those compositions where room temperature cure occurs no further steps need to be taken. Room temperature cure generally occurs with aliphatic amines and amine terminated polyether curing agents. With cyandiamide or dicyandiamide curing agents the coated substrate should be exposed to elevated temperatures to affect cure. Typical elevated temperature curing is effected from 60 °C to 250 °C, preferably from 100 °C to 200 °C, and more preferably from 150 °C to 180 °C.

Another aspect to the present invention is a substrate as described hereinbefore having a coating thereon of a vibration damping coating. Preferably, the thickness of the coating is 1.5 mm or greater and more preferably the coating thickness is 5 mm or less.

The coating of the present invention preferably provides a loss factor of about 10 percent or greater as measured using the composite loss factor test protocol given DIN 53440 (method earlier specified) for 3.9 kg/m<sup>2</sup> applied coating. Generally, the loss factor is 10 percent or greater, and more preferably, 15 percent or greater in the desired operating temperature range.

The present invention is particularly useful for obtaining a risk-label-free composition in vibration damping applications where such a composition is required. In that case, the composition is preferably a combination of at least one saturated thermosettable component such as for example an epoxy resin cured with at least one standard curing agent such as for example an epoxy hardener, that is designed to be risk-label-free according the EEC legislation (as specified above), or epoxy resins and hardeners which after thorough toxicological testing are classified as non-hazardous by skin contact, and blended with thermoplastic interpolymer resins to obtain a wider range of damping over temperature. As discussed above, the compositions may also contain fillers and other adjuncts.

Vibration dampening composition which are not risk-label-free may have limited commercialization in the automotive industry by the fact that the resin formulation is potentially irritant and sensitizing by skin contact.

The automotive industry, especially in Europe, prefers "risk-label-free" systems meaning that the systems do not bear the risk symbol "Xi" nor the risk phrase "R43," and are considered non-hazardous to the workers in case of accidental skin contact.

EXAMPLES

The following examples are provided to illustrate the present invention, but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

5       The pastes described in the Examples of the present invention which follow are made according to the following procedure:

On a lab scale (2-3 kg), approximately 1/3 of the amount of epoxy resin required in the total formulation (liquid component of the paste, acting as binder) is charged into the blade mixer at temperatures that can vary from room temperature (approximately 20  
10 °C) to 50 °C. Then, the solid powder components of the formulation are progressively added to form a very high viscous paste (pre-paste) containing all solid components including the thermoplastic powder, fillers, and epoxy curing agent. This technique (low level of liquid and maximum level of solids) allows to increase the mixing shear which ensures good dispersion and high paste homogeneity. The obtained pre-paste is further  
15 diluted with the rest of epoxy resin and finally a rheology controlling additive such as silica or carbon black is added to the paste to adjust the application viscosity. Vacuum is applied to the paste for about 10 minutes to ensure proper degassing.

20      The test protocol used for measuring vibration damping performance of test coated substrates was according to the method described in DIN 53440, Part 1. About a 2 mm thick coating of the formulation is applied with a caulking gun onto a steel beam of 0.8 mm thick x 12.7 mm wide x 225 mm long. The formulation is equalized to 2 mm with a leveling knife (200 mm coated). The coated beam is cured for 30 minutes to 60 minutes at 150 °C to 200 °C and then mounted in a massive clamp. The cured coated substrate is then  
25 tested at various modes of vibration in the frequency range of approximately 100 Hz - 1500 Hz and over a temperature between -20 °C and 120 °C.

Examples 1-6 and Comparative Example A

Table 1 is the summary of all the compositions of examples used in the present invention. Formulations including different blends of epoxy/ESI were prepared  
30 containing the ingredients expressed in parts by weight as shown in Table 1, and were tested to illustrate their vibration damping performance shown in Table 2 and Figures 1 to 3.

Table 1

Components	Comparative Example A	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
<b>Epoxy Resin A<sup>(1)</sup></b>			37.5	37.5	37.5	37.5	31.61
D.E.R.* 661E <sup>(2)</sup>	7.5	7.5					
D.E.R.* 667 <sup>(3)</sup>	7.5	7.5					
D.E.R.* 732 <sup>(4)</sup>	22.5	22.5					
Dyhard 100s <sup>(5)</sup>	1.78	1.78	1.52	1.52	1.52	1.52	1.15
Dyhard 500 <sup>(6)</sup>	0.69	0.69	0.69	0.69	0.69	0.69	0.15
INDEX* DS 401 <sup>(7)</sup>	0	20	15	19.95	25	30	12.64
CaCO <sub>3</sub> <sup>(8)</sup>	59.05	39.05	44	39.1	34.1	29.1	50.6
Silica/additives <sup>(8)</sup>	0.96	0.96	0.96	0.96	0.96	0.96	1
Carbon Black <sup>(8)</sup>							3

## 5 Notes for Table 1:

<sup>(1)</sup>Epoxy Resin A is the reaction product of D.E.R.\* 330, D.E.R.\* 732, ethyl, triphenylphosphonium acetate catalyst and bisphenol-A in a one-step reaction synthesized as follow: all components except the catalyst are charged to a stirred reactor and heated to 100 °C. The catalyst is added and heating is continued until the reaction mix reaches 160 °C.

10 The temperature is allowed to increase to 170-190 °C by the exothermic reaction. The mixture is maintained at this temperature for about one hour, then cooled down to room temperature. The resulting Epoxy Resin A is a liquid with a viscosity of about 20 Pa.s measured at 35 °C and has an EEW (Epoxy Equivalent Weight) of 450.

<sup>(2)(3)(4)</sup>Epoxy resins commercially available from The Dow Chemical Company.

15 <sup>(5)</sup>Dyhard 100s is a micronized dicyandiamide and is used as a hardener, commercially available from SKW Trostberg.

<sup>(6)</sup>Dyhard 500 is used as a latent catalyst, commercially available from SKW Trostberg.

20 <sup>(7)</sup>INDEX\* DS 401.02 is an ethylene styrene interpolymer (ESI)(Styrene: 70 percent, Ethylene: 30 percent) available from The Dow Chemical Company. The ESI is incorporated into the formulation in a powder form (powder obtained by cryogenic grinding) having an average particle size lower than 200 microns.

<sup>(8)</sup>These materials are used as fillers or additives.

The damping performances of the formulations of Examples 1-6 and Comparative Example A are summarized in Table 2 below and shown in Figure 1, 2 & 3.

25 Table 2 is the summary table of the loss factors measured on all the quoted examples.

Table 2: Loss Factors (percent) as a function of temperature for 3.9 kg/m<sup>2</sup> applied

Temperature (°C)	Comparative Example A	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
0	25.78	25.62				10	
10							13.5
15							16
20	19.6	24.64					18.6
25			21.1	20.6	20.7	20.3	17.1
30			16.7	18.3	19.9	21.6	15
35			13.8	16.1	16.3	20.6	10.8
40	5.7	13.42	9.8	11.9	13.5	15.9	9.3
50						5	
60	1.16	1.6					

The maximum value of the damping factor for the formulation of Examples 1-6 (for 3.9 kg/m<sup>2</sup>) is always superior to 15 percent (around 20 percent), as compared to standard bituminous membranes having a maximum of 15 percent (for 4.5 kg/m<sup>2</sup>).  
5

#### Example 1 and Comparative Example A

A comparison of the damping value of the formulation of Example 1 which contains 20 percent ESI, with the formulation of Comparative Example A which contains no ESI (using the same epoxy and the same epoxy level), is illustrated in Figure 1. Figure 1 shows that the loss factor of the formulation containing ESI is improved over the loss factor of the epoxy resin formulation per se.  
10

#### Examples 2-5

To further illustrate the effect of ESI, several formulations were made according to the procedure explained above. The formulations only differed by the amount of ESI blended into each of the formulations. ESI levels of 15 percent, 19.95 percent, 25 percent and 30 percent were used (Example 2, Example 3, Example 4 and Example 5, respectively). Epoxy Resin A was used and its amount was kept constant at 37.5 percent.  
15

The improvement effect of ESI on the loss factor is quite well illustrated in Table 2 above and shown in Figure 2.

Figure 3 shows that the effective temperature range for a damping factor higher than 10 percent is as wide as 45 °C.

Example 6

Example 6 of the present invention was chosen to demonstrate the typical corrosion resistance of the formulations of this invention.

5       Table 3 shows the typical corrosion resistance performance of a composition of the present invention. Table 3 shows the results of two different tests performed on the cured coating prepared from the formulation of Example 6. In one test, the cured coating was tested for water absorption after exposure of the coating in de-ionized water for 10 days at 55°C. In a second test, the cured coating was tested for corrosion resistance after  
10      exposure of the coating to 100 percent relative humidity at 70°C for 2 weeks. The main result is that, the water absorption is below the automotive specification. No corrosion under the coating is observed after those tests.

Table 3 Corrosion Resistance

Test Conditions	Specification	Result for Example 6
10 days immersion in deionized water, 55°C	Water absorption < 10 percent No corrosion under coating	Water absorption = 4.2 percent No corrosion under the coating
70°C humidity for 7 days & 14 days (H* 7 and H 14)	H 7 : loss of mechanical strength (Lap shear strength) < 25 percent Failure should be cohesive No corrosion H14 : no change versus H7	H0 (Initial) : 3.70 Mpa, - Cohesive failure H7 : 3.04 Mpa, - Cohesive failure, - no corrosion H14 : no change versus H7

15      \*H = humidity.

WHAT IS CLAIMED IS:

1. A vibration damping composition comprising;
  - (a) at least one saturated thermosettable component;
  - (b) a crosslinking agent for the saturated thermosettable component; and
  - 5 (c) a thermoplastic interpolymer resin or blends of interpolymer resins having a glass transition temperature (Tg), as measured by differential scanning calorimetry (DSC), in the range of from -20 °C to 40 °C;  
wherein the saturated thermosettable component upon curing has a Tg, as measured by DSC, of from -20 °C to + 85 °C; and the concentration of the saturated  
10 thermosettable component, the crosslinking agent and the thermoplastic interpolymer resin is sufficient to provide a composition having a loss factor of above 10 percent over a delta temperature range of 50 °C.
2. The composition of Claim 1 wherein the saturated thermosettable component is an epoxy resin.  
15
3. The composition of Claim 2 wherein the epoxy resin is a bisphenol-A epoxy resin.  
20
4. The composition of Claim 3 wherein the number average molecular weight (Mn) of the bisphenol-A epoxy resin is from 350 to 5000.
5. The composition of Claim 2 wherein the epoxy resin is a flexible epoxy resin containing polyether chains selected from the group comprising ethylene oxide, propylene oxide or mixture thereof.  
25
6. The composition of claim 1 wherein the saturated thermosettable component is a blend of epoxy resins from Claims 3 and 5.
7. The composition of any one of Claims 3, 4, 5 or 6 wherein the epoxy resin is present in the composition in an amount of from 20 weight percent to 80 weight percent.  
25
8. The composition of any one of Claims 3, 4, 5 or 6 wherein the epoxy resin has a viscosity from 10 Pa·s to 60 Pa·s at temperature of preparation of the formulation.

9. The composition of Claim 1 wherein the thermoplastic interpolymer resin is a  $\alpha$ -olefin/vinyl aromatic interpolymer.

10. The composition of Claim 9 wherein the  $\alpha$ -olefin/vinyl aromatic interpolymer is an ethylene-styrene interpolymer.

5 11. The composition of Claim 1 wherein the thermoplastic interpolymer resin is present in the composition in an amount of from 20 weight percent to 80 weight percent.

12. The composition of any one of Claims 3, 4, 5 or 6 wherein the crosslinking agent for the epoxy resin is a latent hardener.

10 13. The composition of Claim 12 wherein the latent hardener is dicyandiamide.

14. The composition of Claim 13 wherein the glass transition temperature, as measured by DSC, of the cured epoxy resin is between -20 °C and 85 °C.

15 15. The composition of any one of Claims 3, 4, 5 or 6 wherein the crosslinking agent is present in the composition in an amount of from 1.5 to 0.7 ratio of active epoxy groups to active crosslinking agent group.

16. The composition of Claim 1 wherein the saturated thermosettable component is a polyurethane precursor.

20 17. The composition of Claim 16 wherein the polyurethane precursor is a polyol, polyoxypropylene diols/triols, polyester polyols, polyether polyols, hydroxy functional polyurethane prepolymer and mixtures thereof.

18. The composition of Claim 17 wherein the crosslinking agent is methylene diphenyl di-isocyanate, toluene di-isocyanate or an isocyanate functional polyurethane prepolymer.

25 19. The composition of Claim 1 including one or more fillers.

20. The composition of Claim 18 wherein the filler is CaCO<sub>3</sub>.

21. The composition of Claim 18 wherein the filler is present in the composition in an amount of from 0 weight percent to 65 weight percent.

22. The composition of Claim 1 including a catalyst.

23. The composition of Claim 22 wherein the catalyst is a latent amine catalyst.

24. The composition of Claim 23 wherein the latent catalyst is 2,4-tolylenebis(N,N'-dimethylurea).

5 25. The composition of Claim 23 wherein the latent catalyst is present in the composition in an amount of from 0.05 weight percent to 5 weight percent.

26. The composition of Claim 1 with a maximum loss factor greater than 20 percent.

10 27. The composition of Claim 1 wherein the composition is resistant to metal treatment in an automotive process.

28. The composition of Claim 1 wherein the composition is corrosion resistant.

29. The composition of Claim 1 used as an extrudable vibration deadener for automotive roof, door panels, and side panels.

15 30. The composition of Claim 1 suitable for making objects used as vibration dampers in other than automotive applications including bridges, constructions, and flooring.

31. A vibration damping material which is the cured product of the composition of Claim 1.

20 32. A process for damping vibration of a substrate comprising applying a composition according to Claim 1 to the substrate and curing the composition.

33. The process of Claim 26 wherein the composition is applied to the substrate by spraying a coating of the composition onto the substrate.

25 34. A substrate coated with a composition of Claim 1 wherein the composition provides vibration damping properties.

35. A process for preparing a vibration damping composition comprising blending:

30 (a) at least one saturated thermosettable component having a viscosity lower than 60 Pa.s at temperatures from 10 °C to 60 °C of the blending operation

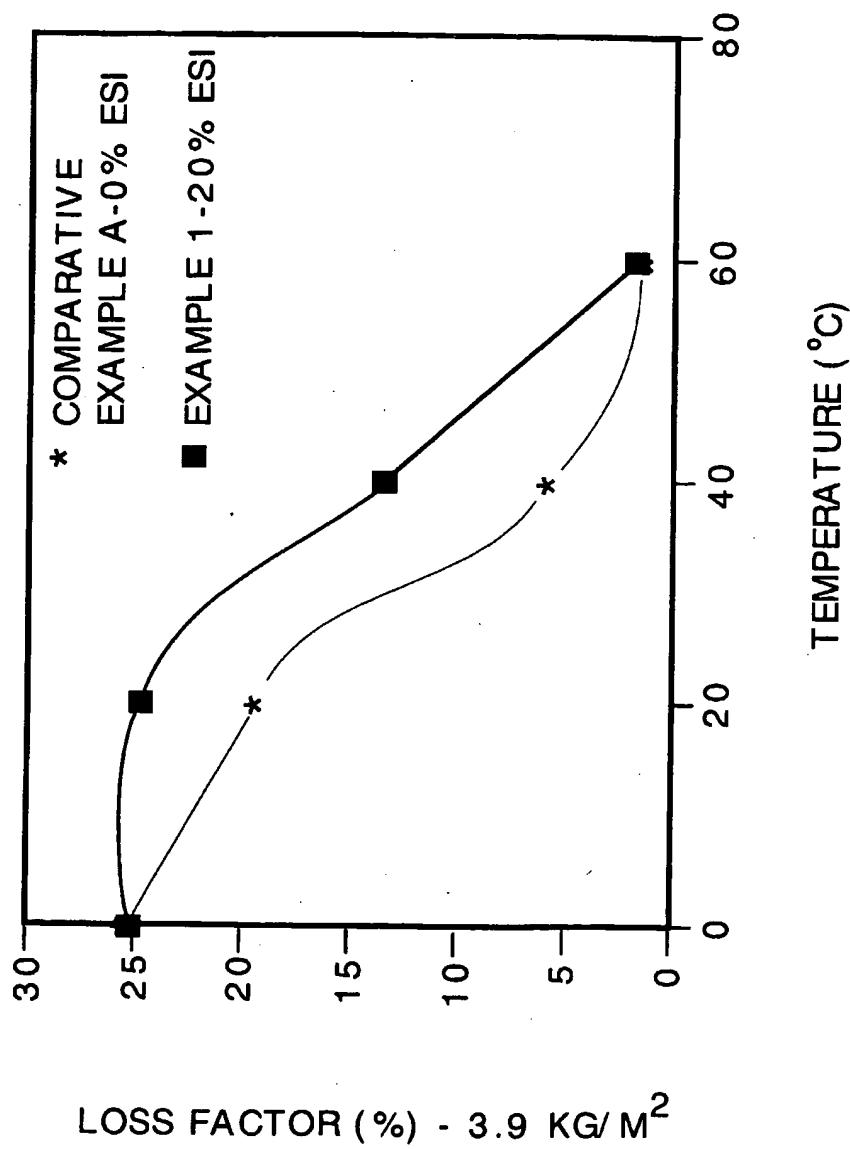
(b) (b) a  $\alpha$ -olefin/vinyl aromatic interpolymer or blend of interpolymers .

36. The composition of any preceding claim wherein the composition is  
in the form of a paste.

37. The composition of any preceding claim wherein the composition is  
5 in the form of a sprayable liquid.

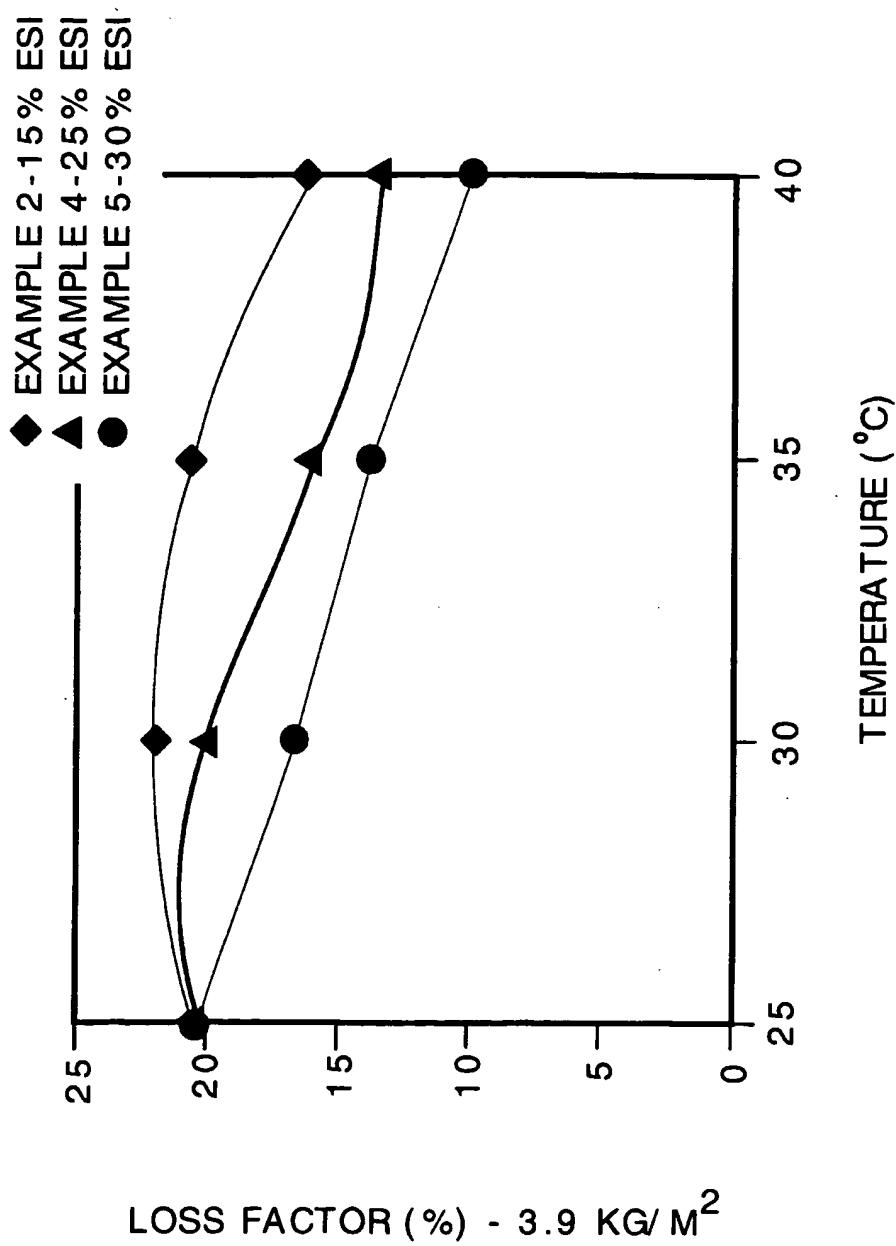
1/3

Fig. 1



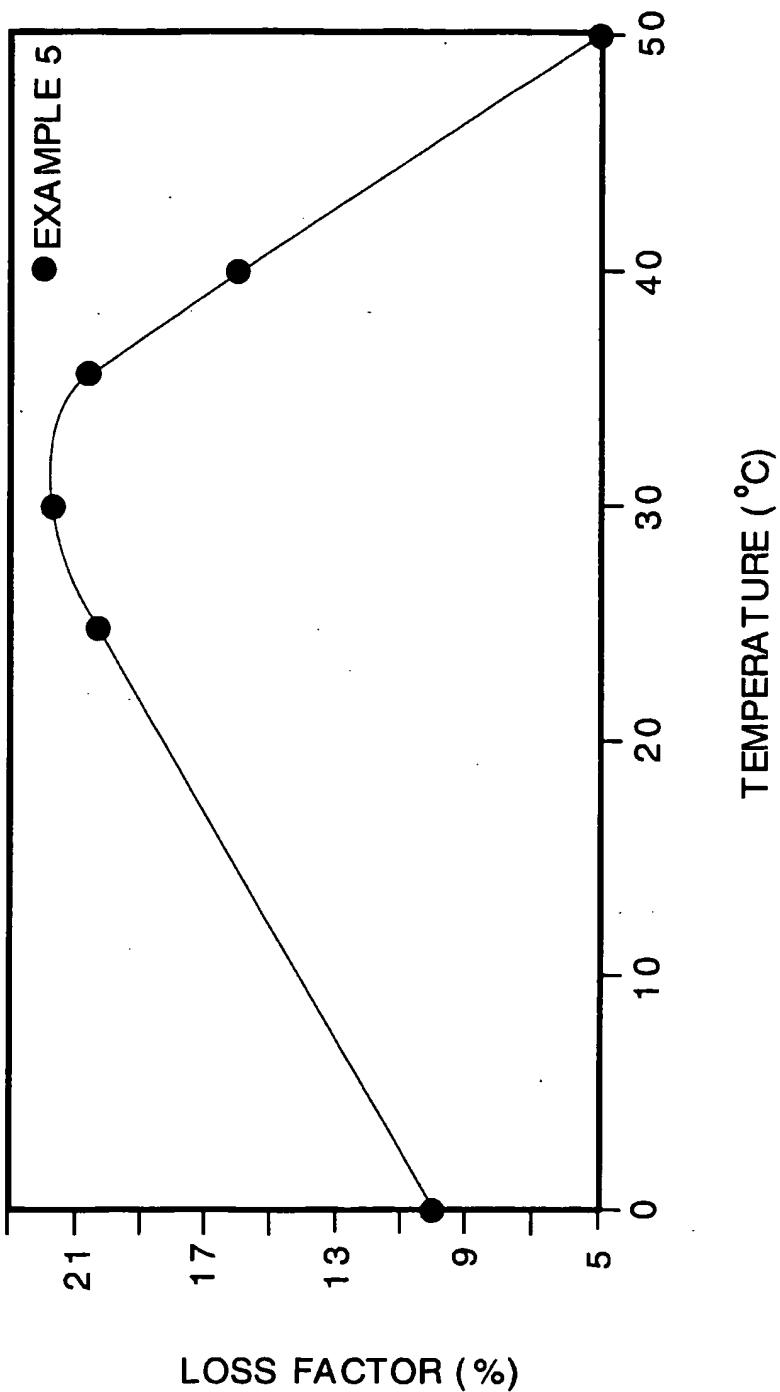
2/3

Fig. 2



3/3

Fig. 3



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
27 June 2002 (27.06.2002)

PCT

(10) International Publication Number  
**WO 02/050184 A3**

(51) International Patent Classification<sup>7</sup>: **C08L 63/00**, (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, C08G 59/22, 59/40 AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, YU, ZA, ZW.

(21) International Application Number: PCT/US01/48718

(22) International Filing Date:  
14 December 2001 (14.12.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/257,321 20 December 2000 (20.12.2000) US

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:  
— *with international search report*

(88) Date of publication of the international search report:  
12 December 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 02/050184 A3**

(54) Title: COMPOSITIONS FOR VIBRATION DAMPING

(57) Abstract: A vibration damping composition including (a) at least one saturated thermosettable component such as a polyurethane precursor, or an epoxy resin having one or more epoxy groups; (b) a crosslinking agent for the saturated thermosettable component; and (c) a thermoplastic interpolymer resin such as a  $\alpha$ -olefin/vinyl aromatic interpolymer, for example an ethylene-styrene interpolymer (ESI); wherein the glass transition temperature of the cured saturated thermosettable component is between -20 °C and +100 °C; and the vibration damping composition provides efficient damping at 0-60 °C with a maximum damping factor >15 percent that is stable at 0-30 °C.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/48718A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08L63/00 C08G59/22 C08G59/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 635 562 A (MALCOLM COLLIN C) 3 June 1997 (1997-06-03) column 5, line 10; claims 2,5,7 claims column 6, line 55 ---	2-15,19, 22-37
Y	US 5 670 006 A (CLARK III HENRY B ET AL) 23 September 1997 (1997-09-23) column 4, line 27-33 column 6, line 1-50; claim 1 column 10, line 40-43 ---	2-37
X	US 6 030 701 A (JOHNSON MICHAEL A ET AL) 29 February 2000 (2000-02-29) column 7, line 10; figure 1A column 10, line 2,3; examples ---	2-8,19, 22,26-37
X	-/-	2-8,19, 22-37

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search

4 June 2002

Date of mailing of the international search report

17.06.02

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/48718

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 16840 A (DOW CHEMICAL CO ;ESSEX SPECIALTY PROD (US)) 8 April 1999 (1999-04-08) the whole document ---	2-37
Y	US 6 153 709 A (XIAO HONG ET AL) 28 November 2000 (2000-11-28) claims -----	2-37

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 01/48718

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 1 because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1

Present claim 1 relates to a composition defined by reference to a desirable characteristic or property, namely the defined compounds (a) to (c) should be "sufficient to provide a composition having a loss factor..."

The claim covers all compositions having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such compositions. In the present case, the claim so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claim also lacks clarity (Article 6 PCT). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the claims startinf from claim 2.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 2-15,19,22-37

A vibration damping composition on the basis of an epoxy resin (a), a crosslinking agent (b) and a thermoplastic interpolymer (c).

2. Claims: 16-18,20-21

A vibration damping composition on the basis of a polyurthane precursor (a), a crosslinking agent (b) and a thermoplastic interpolymer (c).

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 01/48718

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